INL/EXT-05-00450

U.S. Department of Energy FreedomCAR & Vehicle Technologies Program

Advanced Technology Development Program For Lithium-Ion Batteries: Effects of Reference Performance Testing During Aging Using Commercial Cells

July 2005

The INL is a U.S. Department of Energy National Laboratory
operated by Battelle Energy Alliance

INL/EXT-05-00450

Advanced Technology Development Program for Lithium-Ion Batteries:

Effects of Reference Performance Testing During Aging Using Commercial Cells

Jon P. Christophersen
Chinh D. Ho
Chester G. Motloch

David Howell (U.S. DOE)

July 2005

Idaho National Laboratory
Transportation Technology Department
Idaho Falls, Idaho 83415

Prepared for the
U.S. Department of Energy
Assistant Secretary for Energy Efficiency
and Renewable Energy
Under DOE Idaho Operations Office
Contract DE-AC07-05ID14517

ABSTRACT

The Advanced Technology Development Program, under the oversight of the U.S. Department of Energy's FreedomCAR and Vehicle Technologies Program, is investigating lithium-ion batteries for hybrid-electric vehicle applications. Cells are aged under various test conditions, including temperatures and states-of-charge. Life testing is interrupted at regular intervals to conduct reference performance tests (RPTs), which are used to measure changes in the electrical performance of the cells and then to determine cell degradation as a function of test time. Although designed to be unobtrusive, data from the Advanced Technology Development Gen 2 cells indicated that RPTs actually contributed to cell degradation and failure. A study was performed at the Idaho National Laboratory using commercially available lithium-ion cells to determine the impact of RPTs on life. A series of partial RPTs were performed at regular intervals during life testing and compared to a control group that was life tested without RPT interruption. It was determined that certain components of the RPT were detrimental, while others appeared to improve cell performance. Consequently, a new "mini" RPT was designed as an unobtrusive alternative. Initial testing with commercial cells indicates that the impact of the mini RPT is significantly less than the Gen 2 cell RPT.

ACKNOWLEDGMENTS

We thank the following people for their technical and programmatic support:

Michael R. Anderson	DOE-ID
Jim Barnes	DOE-HQ
Tien Duong	DOE-HQ
Kevin Gering	Idaho National Laboratory
Gary Hunt	Idaho National Laboratory (consultant)
Tim Murphy	Idaho National Laboratory
Harold Haskins	USABC (consultant)
Ira Bloom	Argonne National Laboratory
Pete Roth	Sandia National Laboratories
Herb Hess	University of Idaho

CONTENTS

FIGURES

TABLES

ACRONYMS

EIS	electrochemical impedance spectroscopy
FreedomCAR	Freedom Cooperative Automotive Research
L-HPPC	low-current hybrid pulse power characterization
MPPC	minimum pulse power verification
RPT	reference performance test
SOC	state-of-charge

Advanced Technology Development Program for Lithium-Ion Batteries:

Effects of Reference Performance Testing During Aging Using Commercial Cells

1. INTRODUCTION

The U.S. Department of Energy initiated the Advanced Technology Development Program in 1998 to address the outstanding barriers that limit the commercialization of high-power lithium-ion batteries, specifically for hybrid-electric vehicle applications. These barriers include insufficient calendar-life, poor response to abuse, high production costs, and poor low temperature performance. As part of the program, cells are aged under the oversight of the FreedomCAR (Freedom Cooperative Automotive Research) and Vehicle Technologies Program. Aging includes various calendar- and cycle-life tests developed under the Partnership for a New Generation of Vehicles, which was superceded by FreedomCAR in 2002. A full description of the Advanced Technology Development Program within the context of the overall FreedomCAR energy storage research and development is provided in Reference 1.

Reference performance tests (RPTs) are conducted periodically during battery life testing to measure the battery's electrical performance and to determine the degradation in performance due to calendar and cycle aging. Ideally, RPTs should have no impact on cell degradation, but results have indicated otherwise. This study was undertaken to determine the impact of RPTs and to investigate an alternative, less obtrusive test methodology.

2. BACKGROUND

2.1 Gen 2 Cell Testing

Concurrent testing of the second generation of Advanced Technology Development lithium-ion cells (i.e., Gen 2 cells) at the Idaho National Laboratory, Argonne National Laboratory, and Sandia National Laboratories was completed in February 2005. These 18650-size cells (i.e., 18 mm diameter and 65 mm height) consisted of a baseline chemistry and one variant chemistry (identified as Variant C) containing an increased concentration of aluminum dopant in the cathode. The Baseline and Variant C cells were distributed over a test matrix consisting of three states of charge (SOCs) (60, 80, and 100% SOC), four temperatures (25, 35, 45, and 55°C), and three life test protocols (cycle-, calendar-, and accelerated-life testing) in accordance with the cell-specific test plans (References 2 and 3).

Calendar-life testing (performed at Argonne National Laboratory) consists of a voltage clamp at a fixed SOC with a once-per-day pulse profile. Accelerated life testing (performed at Sandia National Laboratories) is the same, but with a different pulse-per-day profile. Both of these tests are defined in Reference 4. Cycle-life testing (performed at Idaho National Laboratory) consists of a repeated application of the 25 Wh Power Assist profile, as defined in Reference 5 and shown in Figure 1. It is a constant power discharge and regen pulse profile with interspersed rest periods (note that the Partnership for a New Generation of Vehicles, now FreedomCAR, convention is to use positive values for discharge and negative values for regen). The cumulative length of a single profile is 72-s and constitutes one cycle. This profile is repeated continuously over a fixed SOC during the cycle-life test, and is nominally charge-neutral, assuming a 90% round trip efficiency. However, a 1-s voltage-controlled discharge step is also usually added to the end of the 9-s discharge power pulse (and a corresponding reduction in the subsequent rest interval) to ensure a stable SOC. The Gen 2 cells were cycled with pulses centered around 60% SOC.

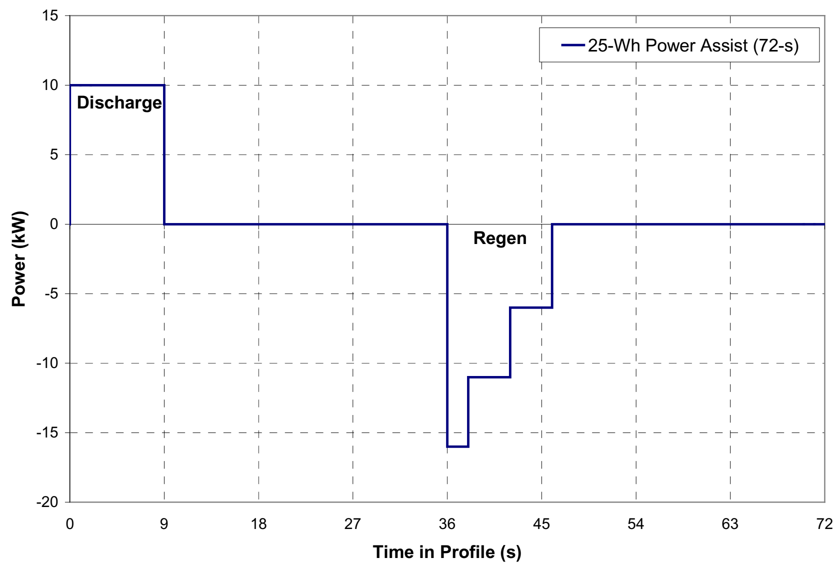

Figure 1. Cycle-life test profile.

The Gen 2 cell life testing was interrupted every 4 weeks (i.e., every 33,600 cycle-life profiles) for reference performance tests (RPTs). These tests are necessary to quantify changes in capacity, resistance, power, and energy as a function of test time. Table 1 shows the RPT sequence for each life test protocol. The accelerated-life cells were subjected to additional testing to help gain a better understanding of changes in cell degradation over life. All RPTs began at 25°C with a fully charged cell. Consequently, after a 4-week period of life testing, the cells were fully discharged to the minimum voltage then charged back to 100% SOC before the start of an RPT. The Gen 2 full charge procedure consists of a constant current charge to the maximum voltage followed by a constant voltage taper charge for a total time of 2.5 hours (References 2 and 3).

Table 1. RPT Sequence for each Life-Test Protocol

Calendar-Life	Cycle-Life	Accelerated-Life
$C_1/1$ discharge	$C_1/1$ discharge	5 $C_1/1$ discharges
$C_1/25$ discharge	$C_1/25$ discharge	$C_1/25$ discharge
$C_1/25$ charge	$C_1/25$ charge	-
EIS at 60% SOC	EIS at 60% SOC	EIS at 60% SOC
-	-	EIS at 100% SOC
-	-	2 $C_1/1$ discharges
-	-	$C_1/10$ discharge*
L-HPPC	L-HPPC	L-HPPC
-	-	0°C L-HPPC**

* Initiated after the 8-week RPT
** Discontinued after the 24-week RPT

The $C_1/1$ and $C_1/25$ static capacity discharge tests consist of a constant current discharge to the minimum voltage from a fully charged state using a fraction of the rated capacity defined at the 1-h rate (i.e., subscript "1"). For example, the Gen 2 Baseline and Variant C cells were rated at 1.0 and 0.8 Ah, respectively, at the C_1 rate (Reference 2). Consequently, the Baseline cell $C_1/25$ test would result in a discharge (or charge) current of 1.0/25, or 40 mA. Similarly, the Variant C $C_1/25$ test current would be 0.8/25, or 32 mA. The $C_1/1$ test current would be 1.0 and 0.8 A for the Baseline and Variant C cells, respectively.

The low-current hybrid pulse power characterization (L-HPPC) test is the most important component of the RPT because it provides information on pulse power capability and available energy for direct comparisons with the Partnership for a New Generation of Vehicles goals (Reference 5). The L-HPPC profile, shown in Figure 2 and defined in Reference 5, consists of a constant current discharge and regen pulse with a 32-s rest period in between. The 18-s discharge pulse is performed at a $5C_1$ rate, and the 10-s regen pulse is at 75% of the discharge rate. This profile is repeated at each 10% depth-of-discharge increment, with a 1-h rest at open circuit voltage to ensure that the cells have reached electrochemical and thermal equilibrium. The Partnership for a New Generation of Vehicles goals are based on an 18-s discharge and 2-s regen pulse resistance, which are calculated from the ratio of the change in voltage (ΔV) divided by the change in current (ΔI) at each 10% depth-of-discharge increment. From the resistance data, the discharge and regen pulse power capabilities are calculated, and then related to corresponding amount of energy discharged at a $C_1/1$ rate to determine available power as a function of cumulative energy removed.

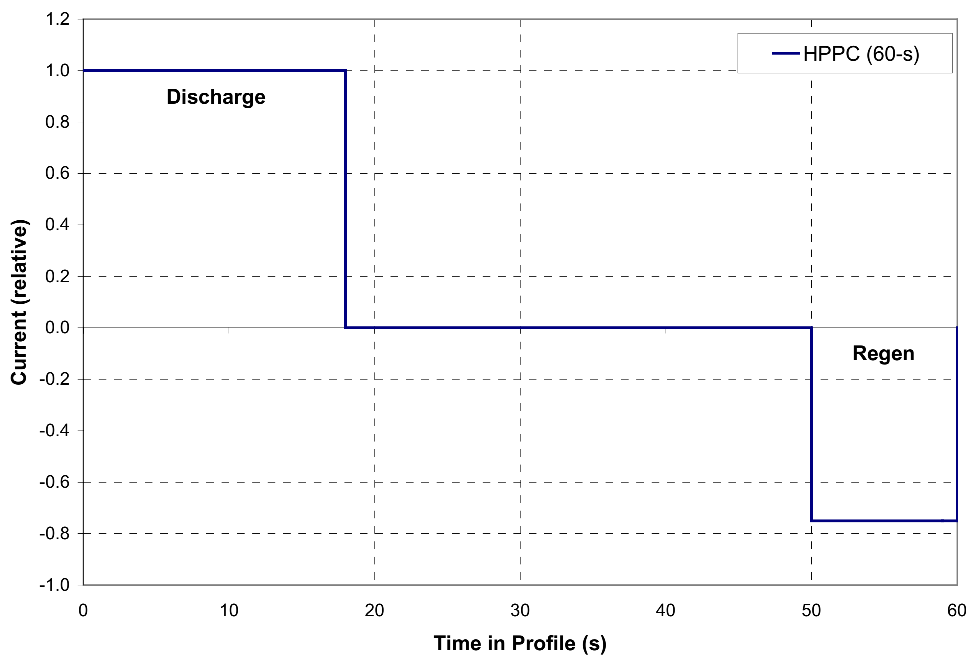

Figure 2. L-HPPC profile.

Electrochemical impedance spectroscopy (EIS) is a method used to determine impedance changes in the electrode-electrolyte interface using equivalent circuit models (Reference 6). Although it is not included in the standard Partnership for a New Generation of Vehicles RPT (Reference 5), it was added to the Gen 2 sequence as an exploratory test. Since EIS measurements are very benign (no charging or discharging required), this methodology was investigated as a possible alternative measurement of degradation. The Gen 2 cell EIS was performed at 60% SOC (and 100% SOC for the accelerated-life cells) over a frequency range of 10 kHz to 10 mHz following an 8 to 12-h rest at open circuit voltage to ensure electrochemical equilibrium. The impedance was measured using a four-terminal connection, and with a minimum of eight points per decade of frequency.

Results from the RPTs are used to calculate degradation in capacity, impedance, and power. *Capacity fade* is the percent loss in $C_1/1$ discharge capacity, and *power fade* is the percent loss in available power over a precise energy range of 300 Wh, as calculated from the L-HPPC test (Reference 5). These fades are normalized to the beginning-of-life RPT (i.e., the beginning-of-life capacity and power fades are both 0%).

2.2 Gen 2 Data Analysis

Figure 3 shows the cycle-life 9-s discharge and 2-s regen pulse resistances from a representative Gen 2 Baseline cycle-life cell. This cell was cycled for 136 weeks (~1140k cycles) at 25°C and showed 34% capacity fade and 51% power fade. The pulse resistance suddenly drops every 672 hours (in conjunction with an RPT), then quickly recovers. Similar trends were also observed with the Baseline and Variant C cells cycle-life tested at 45°C, and for the calendar- and accelerated-life cell groups. This indicates that the RPT has a temporary "healing" effect on pulse resistance.

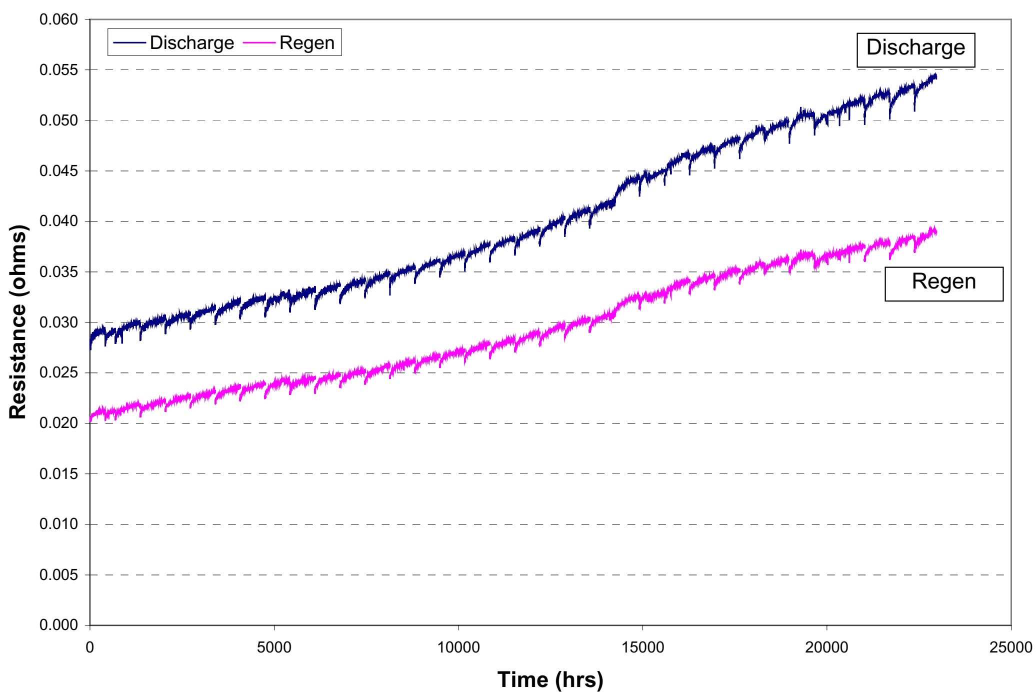

Figure 3. Pulse resistance for a representative 25°C Baseline cell aged for 136 weeks.

Figure 4 shows the average power fade as a function of test time for the calendar- (circles), cycle- (squares), and accelerated- (triangles) life cells, all of which were aged at 45°C and 60% SOC. The calendar-life cells consistently show less power fade than the cycle-life cells. Since the RPTs are the same (see Table 1), this demonstrates that continuous pulsing is more stressful than a pulse-per-day followed by a voltage clamp. The accelerated-life cells, however, show a significantly greater fade rate. Since the accelerated-life cells were tested similarly to the calendar-life cells, i.e., a pulse-per-day test followed by a voltage clamp, the increased degradation should be primarily attributable to other factors such as the RPTs. As shown in Table 1, the accelerated-life cells had several additional tests every 4 weeks. Similar results were seen at the other test temperatures as well. These data suggest that the RPTs are not as unobtrusive as previously assumed. Consequently, a study was conducted at the INL to investigate the effects of RPTs on cell aging.

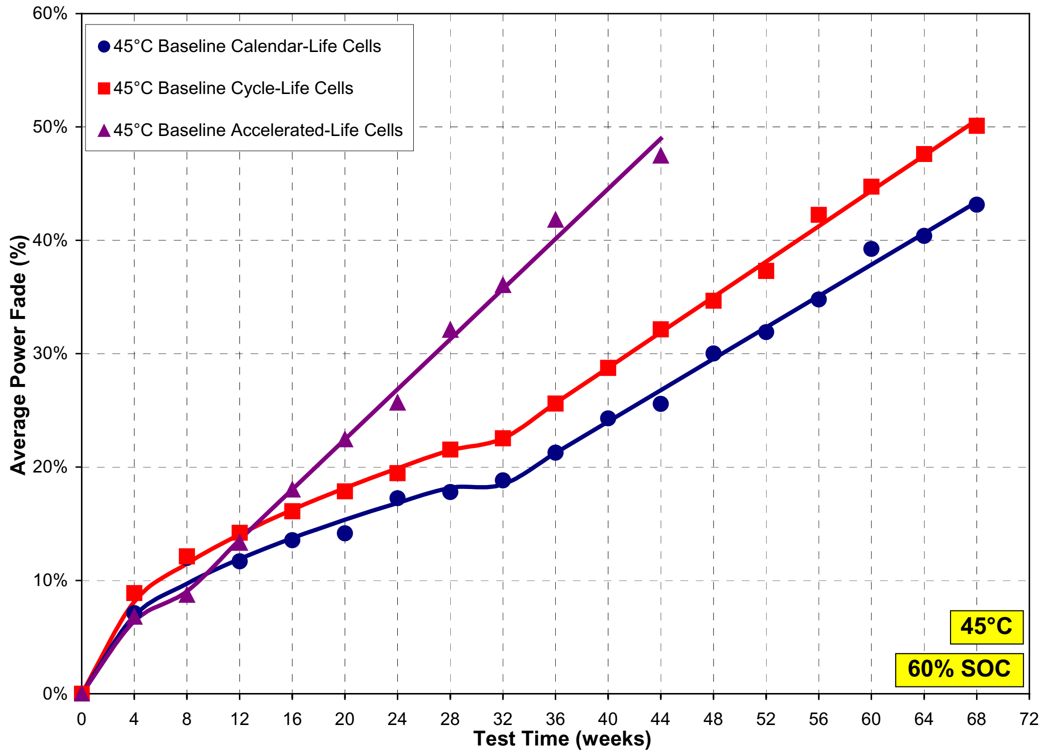

Figure 4. Available power fade for the 45°C life test conditions

3. EXPERIMENTAL

3.1 Test Setup

INL purchased 24 commercially available prismatic cells (i.e., PowerfLite cells) for this study (see Figure 5). They have a $LiCoO_2$ cathode and a graphite anode with $LiPF_6$ salt in EC/DEC/DMC electrolyte. Based on initial static capacity discharge tests, they were rated at 1 Ah at the C_1 rate over a voltage range of 4.2 to 2.75 V. Although these cells are not representative of the current FreedomCAR technologies, they are useful for investigative purposes. The cells were tested in an environmental chamber able to control ambient temperature within ± 3°C (Reference 2). They were also placed in aluminum thermal blocks, as shown in Figure 6, to enable more uniform temperature control and minimize temperature transients (Reference 4). The blocks were originally designed for 18650-size cell testing (i.e., Gen 2 cells), but were adapted to fit the prismatic cells. Thermocouples were also placed on each cell to monitor temperature. The voltage and current sense leads were soldered into ⅛- by ¼-in. brass connectors and attached to the cell tabs. Thin vellum insulators were used on the negative tab for electrical isolation (see Figure 6). This enabled the brass connectors to be attached close to the cell and minimize tab impedance.

Figure 5. PowerfLite cells

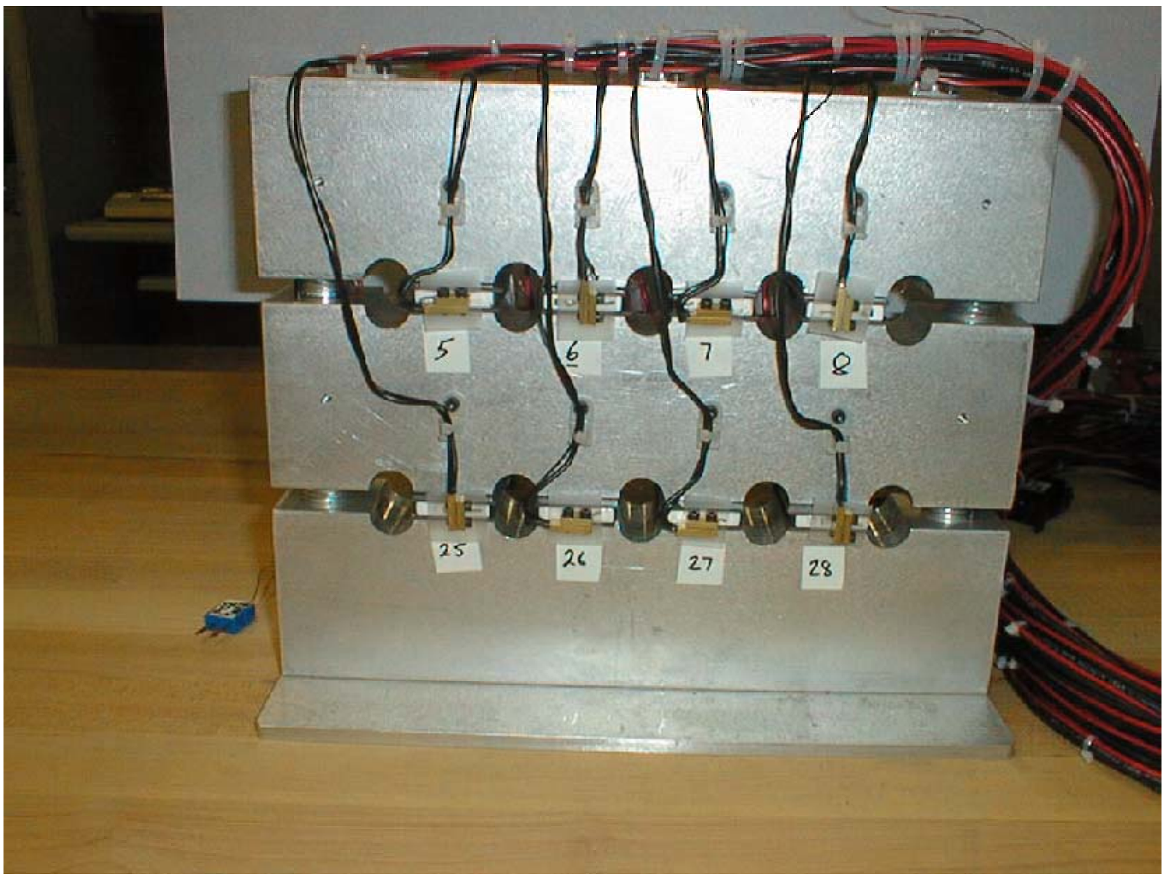

Figure 6. PowerfLite cells in a thermal block.

3.2 Test Procedure

The test procedure for this study is provided in Appendix A. The RPT sequence outlined in Table 1 was split into various partial RPT groups. Cycle-life testing was conducted at 60% SOC and 25°C using the Gen 2 cycle-life profile (Figure 1) with partial RPTs every 2 weeks (16.8k cycles). The partial RPTs are listed in Table 2, and are compared to a control group having no RPT interruptions.

Table 2. PowerfLite Cell Partial RPT Setup

# of Cells	Partial RPT	Description
4	Control	Cycle-life aging with no RPTs
3	Multiple Capacity	Seven $C_1/1$ and one $C_1/25$ discharge
3	Single $C_1/1$	One $C_1/1$ discharge
4	60% EIS	EIS measurements at 60% SOC
3	100% EIS	EIS measurements at 100% SOC
4	25°C L-HPPC	$C_1/1$ and L-HPPC at 25°C
3	0°C L-HPPC	$C_1/1$ and L-HPPC at 0°C

Except for the 0°C L-HPPC group, all partial RPTs were conducted at 25°C. Each discharge in the multiple capacity group (including the $C_1/25$ discharge) was followed by a $C_1/1$ charge. As with Gen 2 testing, the PowerfLite cells were fully discharged then charged back to 100% SOC before the start of an RPT (using a constant voltage taper for a total charge time of 2.5 hours). At the end of an RPT, the cells were once more fully charged, then taper discharged to 60% SOC (using a constant voltage clamp until the current fell below 10 mA) prior to the next 2 weeks of cycle-life testing.

The partial RPT cell groups were cycled for 12 weeks (~100k cycles), which corresponds to approximately 15 weeks (~130k cycles) of aging for the control cell group having no RPT interruptions. Each group of cells was subjected to a full $C_1/1$ and L-HPPC at beginning and end of test to gauge the overall capacity and power fade at end of test.

4. RESULTS

4.1 Cycle-Life Pulse Resistance Data

Figure 7 shows the average cycle-life discharge pulse resistance for the control cell group. The cycle-life pulse resistance data from each partial RPT group have been normalized to the control cell group such that the first 2-week set matches the control cell data, allowing for direct comparisons. Due to a programming glitch, the control cells were also stopped after the first 2 weeks of aging, followed by a full discharge and charge. The cells were subsequently discharged back to 60% SOC and cycled without interruption. This resulted in a sudden drop in pulse resistance followed by a quick recovery, as was seen with the Gen 2 cells. This indicates that the discontinuities in pulse resistance following an RPT is primarily due to the steps taken prior to the actual RPT (i.e., a full discharge and charge) and not necessarily the RPT itself.

Figure 8 shows the normalized average discharge pulse resistances for the multiple capacity and the single $C_1/1$ partial RPT groups compared to the control cells. As expected, the pulse resistance shows a discontinuity after each RPT. The single $C_1/1$ group consistently recovers to the same level as the control cells and does not appear to have a long-term impact on pulse resistance. Although the multiple capacity group initially shows similar results to the single $C_1/1$ group, it has a delayed negative impact with greater resistance values after 8 weeks of aging (~1750 hours). This is not surprising, since multiple discharges and charges are equivalent to a "mini" cycle-life test every RPT, and the cumulative effect should lead to faster degradation rates. The Gen 2 calendar- and cycle-life cells were subjected to an equivalent of four full discharges and charges at each RPT. This includes both the $C_1/1$ and $C_1/25$ static capacity tests and the various charges and discharges required to start the next test in the RPT sequence. The accelerated-life cells were subjected to the equivalent of twelve full discharges and charges at each RPT, and, consequently, faded much faster (see Figure 4).

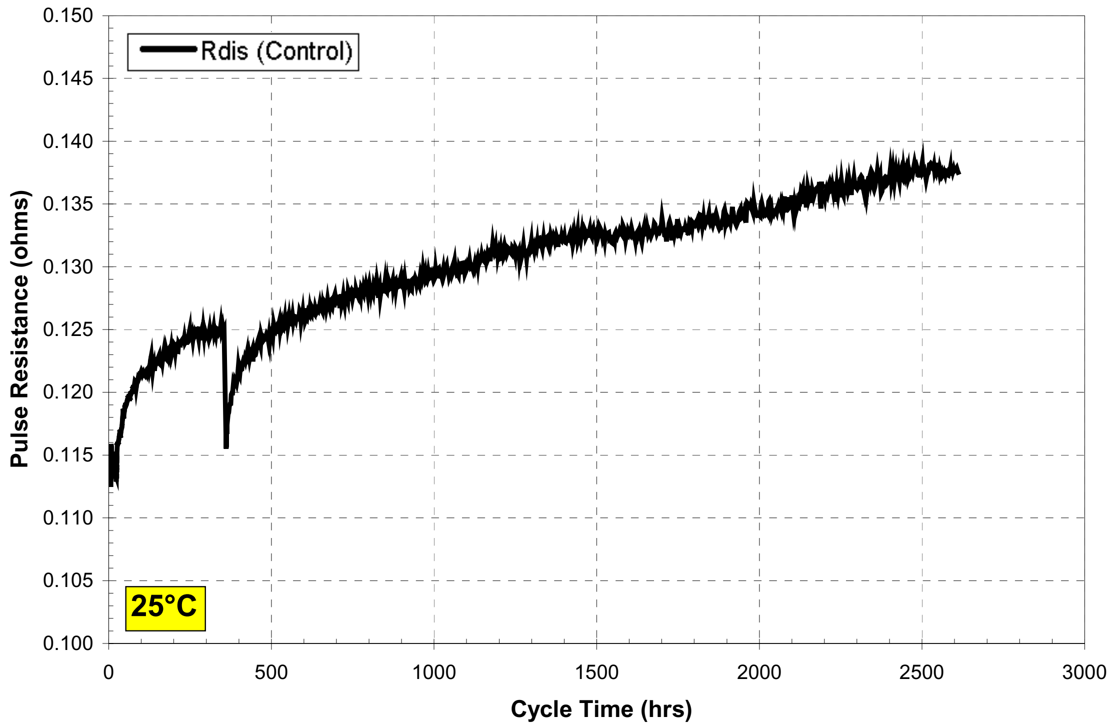

Figure 7. Cycle-life pulse resistance for the control cells

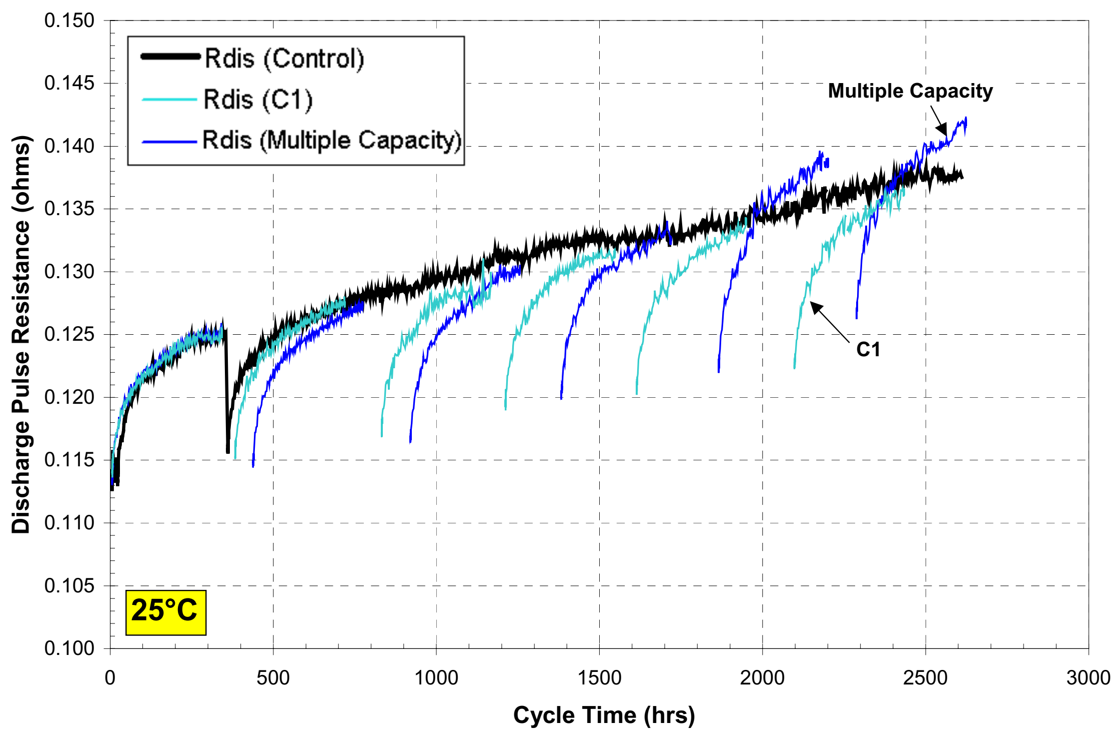

Figure 8. Cycle-life pulse resistance for the capacity partial RPT groups

Figure 9 shows the normalized average discharge pulse resistances for the L-HPPC groups at both 25 and 0°C compared to the control cells. As stated above, each L-HPPC test was preceded by a single $C_1/1$ discharge, which has no impact on pulse resistance (see Figure 8). The 25°C L-HPPC group appears to improve cell performance, since the pulse resistance after 12 weeks is less than the control cells. At 0°C, however, there is a delayed negative impact on performance. Initially, the 0°C L-HPPC appeared to improve performance, but the resistance growth rate started to increase more rapidly during the 8-week cycle-life period. The sudden drops in pulse resistance at the end of the 6- and 8-week cycle-life sets (~ 1100 and 1500 hours, respectively) are due to problems with the environmental chamber. It was having difficulty maintaining 25°C, and increased to as high as 26.8°C, thus reducing pulse resistance. The trend, however, clearly shows an increased growth rate. The deleterious impact of the 0°C L-HPPC test is not surprising, since pulsing at lower temperatures can result in lithium unavailability due to several possible mechanisms such as phase transitions or lithium plating on the anode (Reference 7).

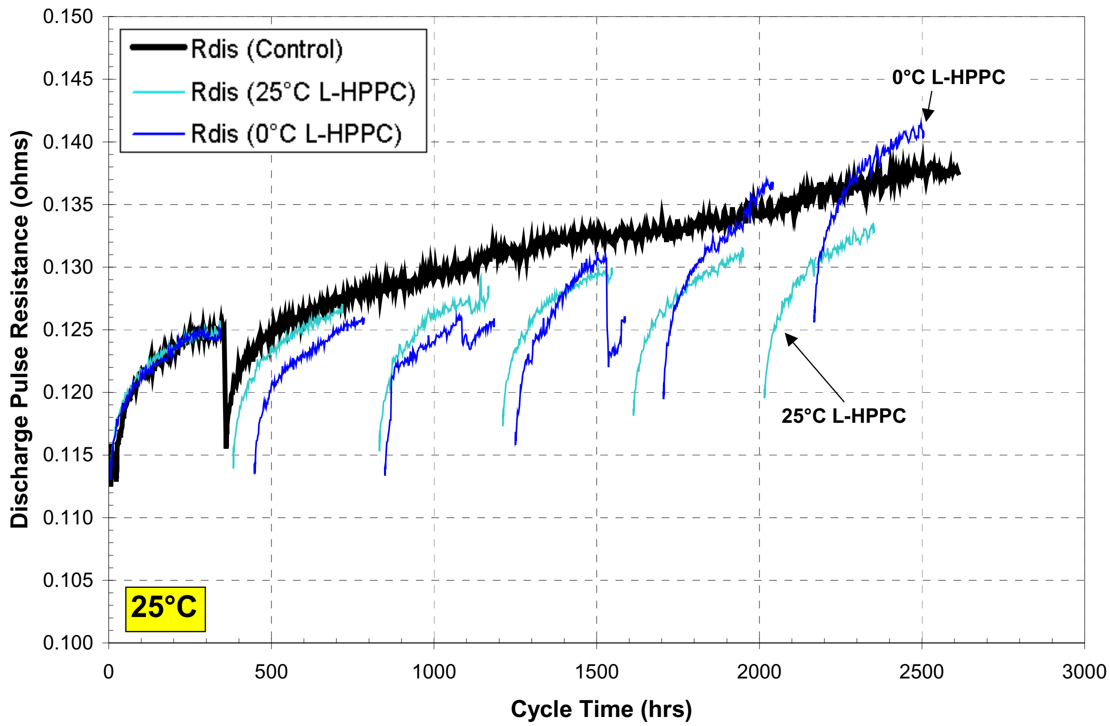

Figure 9. Cycle-life pulse resistance for the L-HPPC partial RPT groups

Figure 10 shows the average normalized discharge pulse resistances for the EIS groups at both 60 and 100% SOC compared to the control cells. The 100% SOC EIS group does not appear to impact pulse resistance, but the 60% SOC EIS shows an improvement. Figures 11 and 12 show the average EIS Nyquist curves for 60 and 100% SOC, respectively (for logistical reasons, the 10-week EIS measurements could not performed). The electrolyte resistance (R_E) is apparently independent of SOC, showing approximately 45 mΩ at each SOC. The charge transfer resistance (R_{CT}), however, shows more growth at 100% SOC (~ 10%) than at 60% SOC (~ 7%), indicating that higher SOCs result in greater cell degradation. This is consistent with what was seen for the Gen 2 accelerated-life cells aged at 60, 80, and 100% SOC (Reference 4). Therefore, although EIS measurements are the most benign component of the RPT (no charging or discharging involved during testing), the SOC at which measurements are taken can have an impact on pulse resistance, as seen in Figure 10.

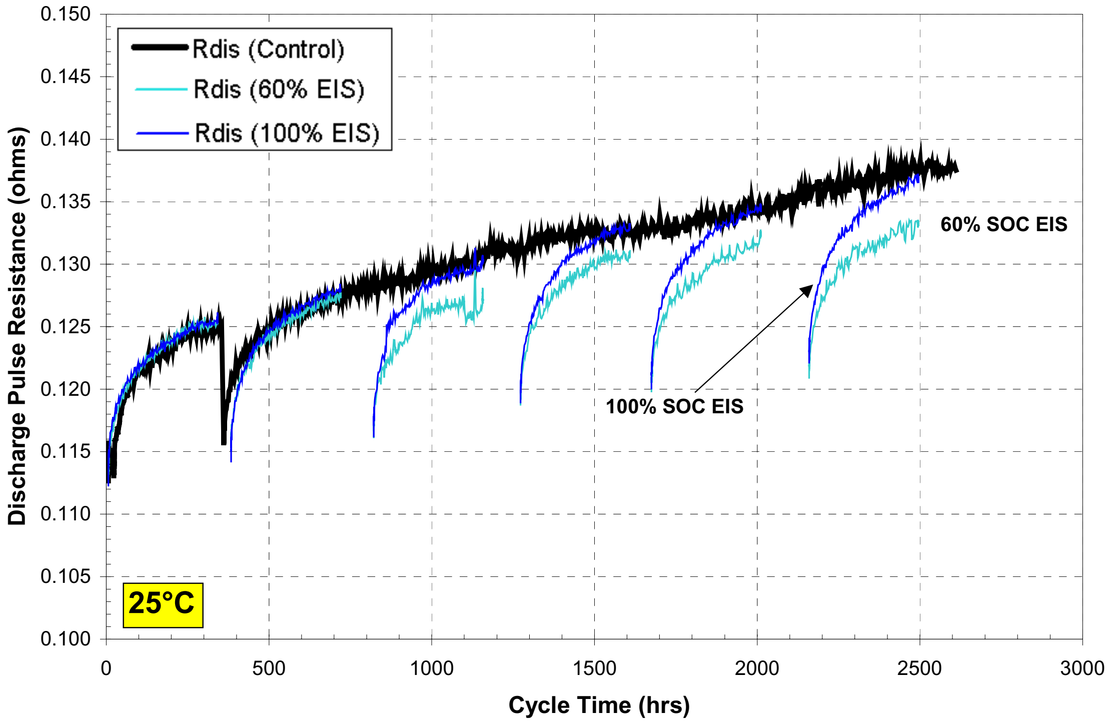

Figure 10. Cycle-life pulse resistance for the EIS partial RPT groups

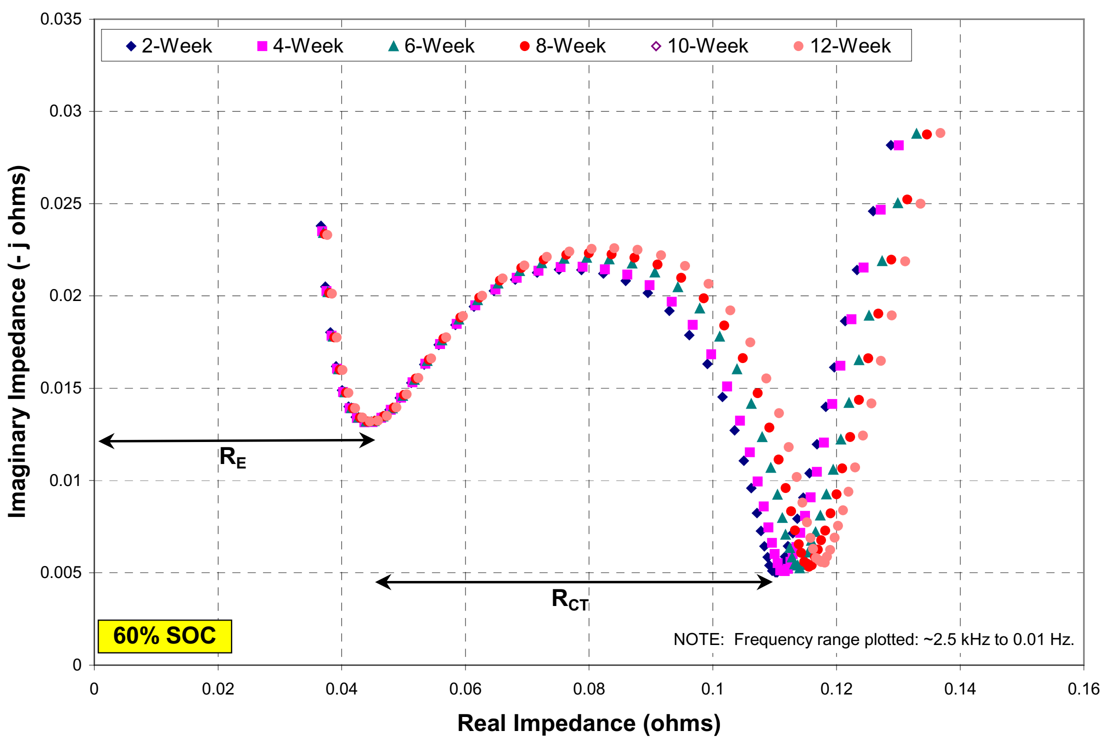

Figure 11. Average EIS measurements for the 60% SOC EIS groups

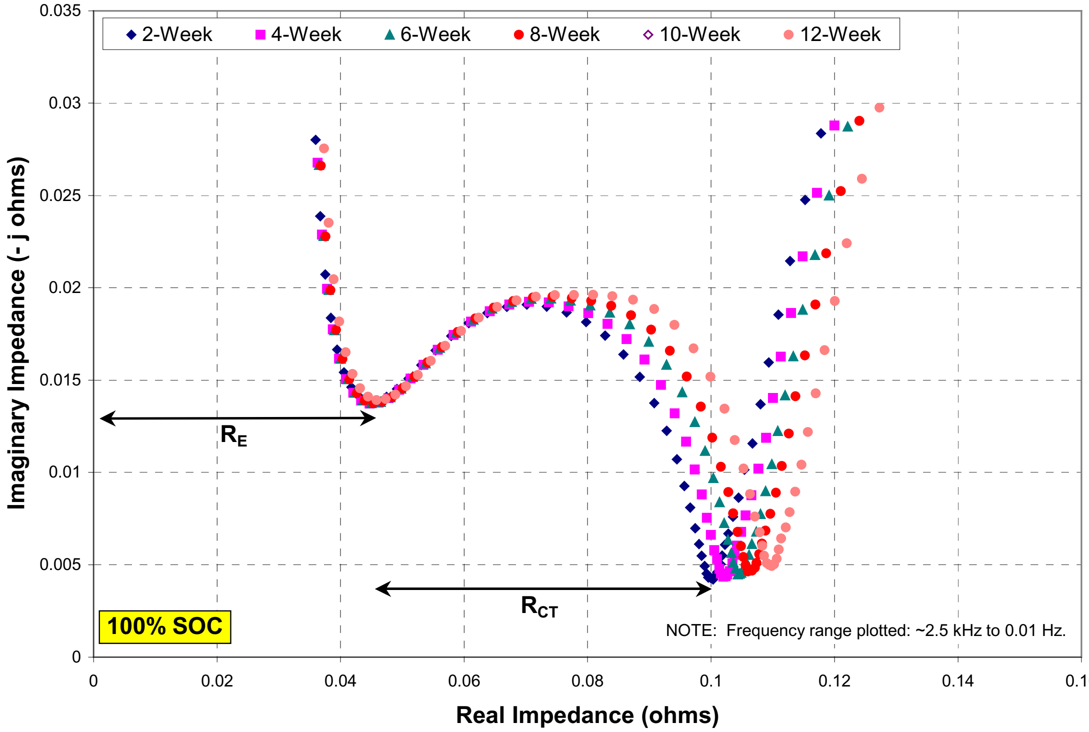

Figure 12. Average EIS measurements for the 100% SOC EIS groups

4.2 RPT Data

Figure 13 shows a summary of the capacity and power fade of each group at end of test. Interestingly, the capacity fade and power fade generally show similar trends for each group. Capacity is a measure of the number of coulombs available for transfer between the electrodes and power is a measure of the rate of that transfer. These results clearly show that the two are somewhat coupled.

The most damaging component of the RPT is the multiple capacity group, with 17.0% power fade and 6.4% capacity fade. Since all of the Gen 2 life test groups were subjected to multiple capacity tests every 4 weeks (4 for the calendar- and cycle-life cells and 12 for the accelerated-life cells), they were indeed impacted by the RPTs. The 0°C L-HPPC test also contributed to increased degradation rate for the Gen 2 accelerated-life cells. The corresponding partial RPT group showed a significantly greater capacity fade than the other partial RPT groups and one of the larger power fades.

Although the single $C_1/1$ partial RPT group did not appear to impact pulse resistance (see Figure 8), it did show a greater power fade than the control cells. Interestingly, the 25°C L-HPPC partial RPT group (which was preceded by a $C_1/1$) showed less capacity and power fade than the single $C_1/1$ partial RPT group. This indicates that the L-HPPC test is beneficial to cell performance.

Both the 100 and 60% SOC EIS groups show less capacity fade than the control cells. The 60% SOC EIS group also shows very similar power fade to the control cells. As was seen with the pulse resistance, the 100% SOC group shows more degradation than the 60% SOC group. The difference in power fade (~3.5%) is very similar to the difference in R_{CT} growth (~3.0%).

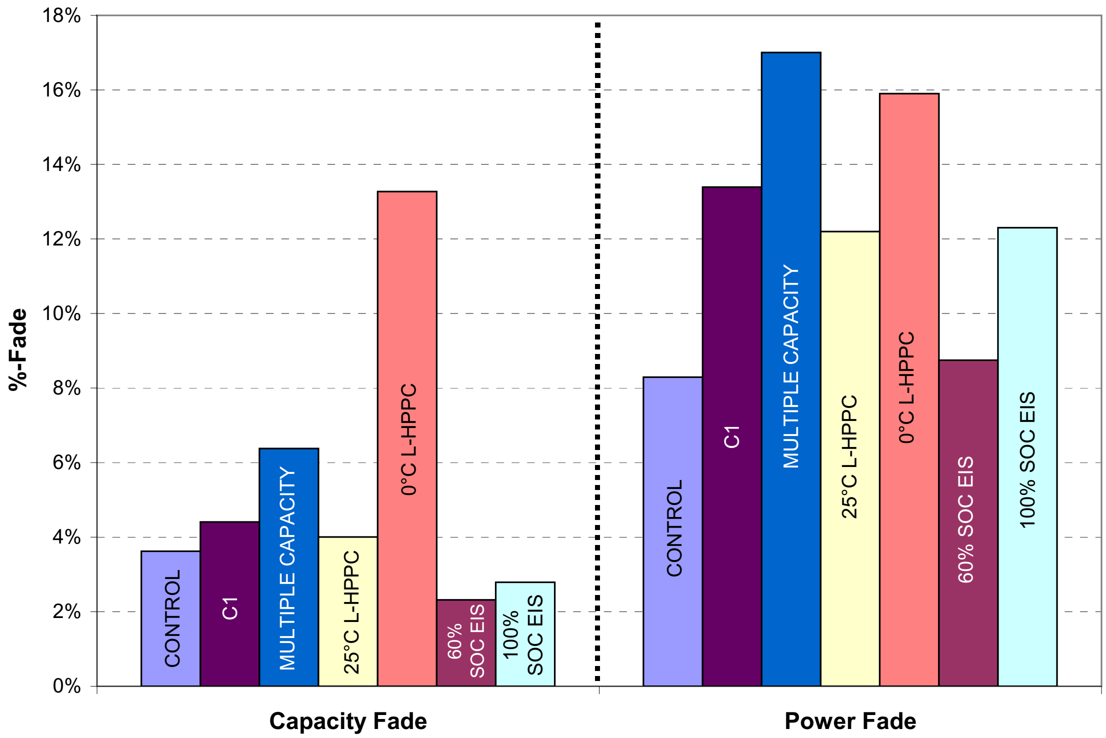

Figure 13. Average capacity and power fade for each partial RPT group

5. NEW REFERENCE PERFORMANCE TEST

Based on this study, a new reference performance test needs to be developed for future cell aging. It should eliminate all full discharges and charges to minimize the post-RPT pulse resistance discontinuity (see Figure 7). Also, it should include L-HPPC profiles primarily because they provide the most information directly comparable with the FreedomCAR goals with minimal adverse impact on cell life (as shown in Figures 9 and 13). EIS measurements could also be considered, but they do not provide much additional relevant information and take a significantly longer amount of time.

5.1 Minimum Pulse Power Characterization

The minimum pulse power characterization (MPPC) test was designed for the Battery Technology Life Verification Test Manual (Reference 8). This manual was prepared to help developers successfully commercialize advanced battery systems for automotive applications. The goal is to verify the required 15-year life capability at a target confidence level of 90% within one or two years of testing. This requires an RPT that is as unobtrusive as possible while still providing sufficient information on cell degradation for accurate life prediction. The MPPC was designed to meet these criteria while also minimizing the time off life testing.

The new MPPC profile is shown in Figure 14 and defined in Reference 8. It consists of only two L-HPPC pulse profiles, with a $C_1/1$ taper discharge in between. Note that the L-HPPC profile used in the MPPC is based on the new FreedomCAR Manual (Reference 9), which is similar to Figure 2, but with a 10-s discharge and regen pulse and a 40-s rest in between. This profile is performed at two SOC conditions known as SOC_{MAX} and SOC_{MIN}, which are reference conditions representing the anticipated standard operating range for a battery system (typically specified by the manufacturer, e.g., 80 and 40% SOC, respectively). The battery will normally be life tested at one of these SOCs as well. One significant advantage of the MPPC is that it is first performed at the elevated life test temperature, and then repeated at room temperature. This allows life predictions to be based on temperature-compensated data. A disadvantage of the MPPC is the inability to acquire accurate power data at the target FreedomCAR goal of 300 Wh. All life predictions are based on resistance.

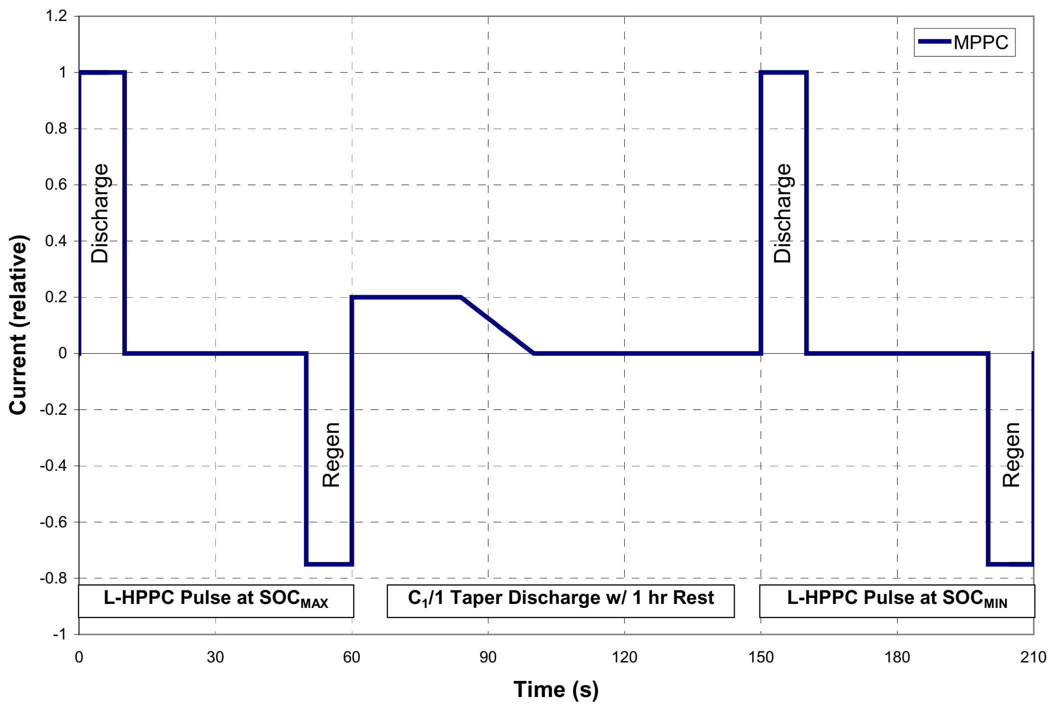

Figure 14. MPPC profile

5.2 MPPC Experimental Setup

The PowerfLite prismatic cells were used for a preliminary verification of the MPPC. The test matrix is shown in Table 3. The maximum and minimum SOCs for these cells were 80 and 40%, respectively. All six cells were cycled using the Gen 2 cycle-life profile (Figure 1) at 30°C and SOC_{MAX}, with three cells subjected to "full" RPTs (C_1/1 and L-HPPC test), while the other three were subjected to "mini" RPTs (MPPC test). The RPTs were initially every 2 weeks, but were extended to 4-week intervals after 6 weeks of aging to determine any long-term impact of the RPT. Note that at the time of this testing, the Technology Life Verification Test Manual was still under development, and the PowerfLite cells were subjected to a slightly different version of the MPPC. It consisted of the L-HPPC profile shown in Figure 2 with a C_1/3 discharge to SOC_{MIN} from SOC_{MAX} without any tapering.

Table 3. PowerfLite cell MPPC test setup

# of Cells	RPT	Description
3	Full	C_1/1 and L-HPPC
3	Mini	MPPC

5.3 MPPC Cycle-Life Results

Figure 15 shows the cycle-life pulse resistance for both RPT groups. The mini RPT pulse resistance was normalized to the full RPT data for direct comparisons. Since testing began with a full RPT for both groups, it's not surprising that the initial (0-h) drop in resistance is similar. Due to a programming glitch after the first 2 weeks of aging (~ 340 hours), both groups were also fully discharged and charged prior to the start of the RPT. Consequently, the drop in pulse resistance is also similar for both groups at the start of the 4-week cycle-life period. Following the 4-week RPT, however, a noticeable improvement in the post-RPT discontinuity is seen for the mini RPT group. The mini RPT group shows approximately half of the drop in pulse resistance than the full RPT group. Also, once the cycle-period was increased to 4 weeks, the slope of the mini RPT group is clearly less than the full RPT group, indicating that the MPPC is beneficial to cell performance.

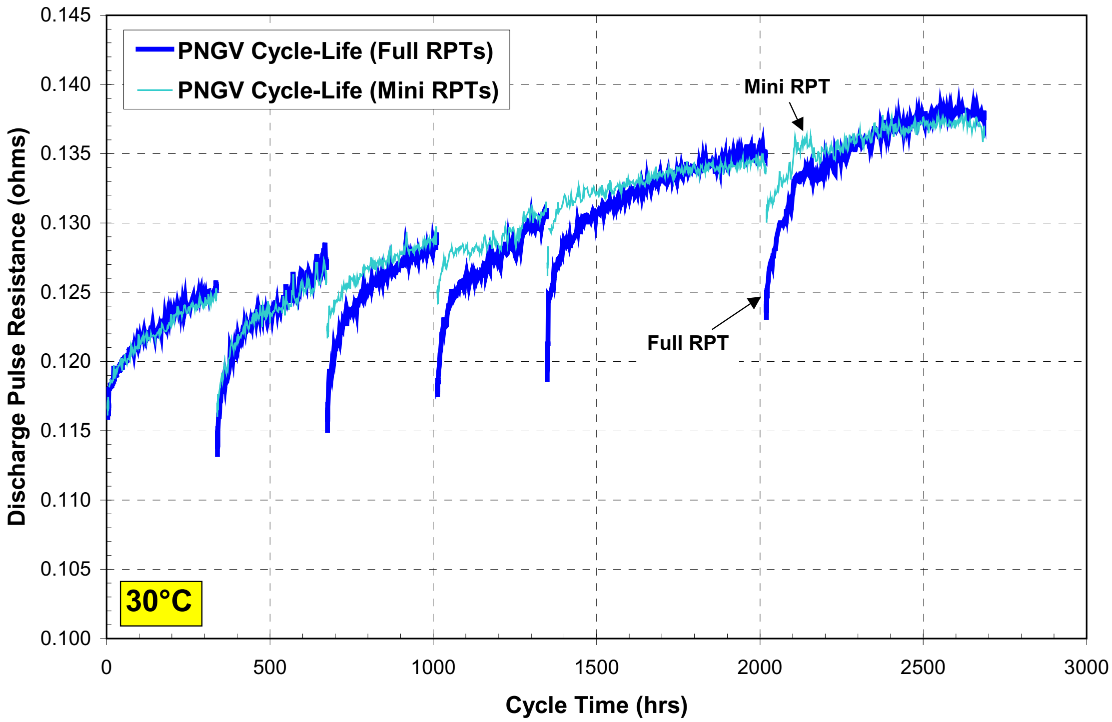

Figure 15. Cycle-life pulse resistance for the full and mini-RPT groups

5.4 MPPC RPT Results

Figure 16 shows the average capacity and power fade for each RPT group after 16 weeks of aging. The capacity fades are virtually identical, but the mini RPT power fade is slightly less than the full RPT group. This indicates that the MPPC is not adversely impacting the overall cell performance. Figure 17 shows the corresponding average growth in discharge resistance at both SOC_{MAX} and SOC_{MIN}. The full RPT resistance growth was determined from a linear interpolation to the appropriate voltage since the L-HPPC test is based on depth-of-discharge (Reference 5). Interestingly, the mini RPT resistance growth at SOC_{MAX} is larger than the full RPT group, but the opposite is true at SOC_{MIN}. Also, whereas the full RPT resistance growth at SOC_{MAX} is slightly less than at SOC_{MIN}, the mini RPT resistance growth is significantly greater at SOC_{MAX}, demonstrating that the MPPC test causes different impedance behavior. These observations need to be investigated more thoroughly, particularly with respect to its impact on life predictions.

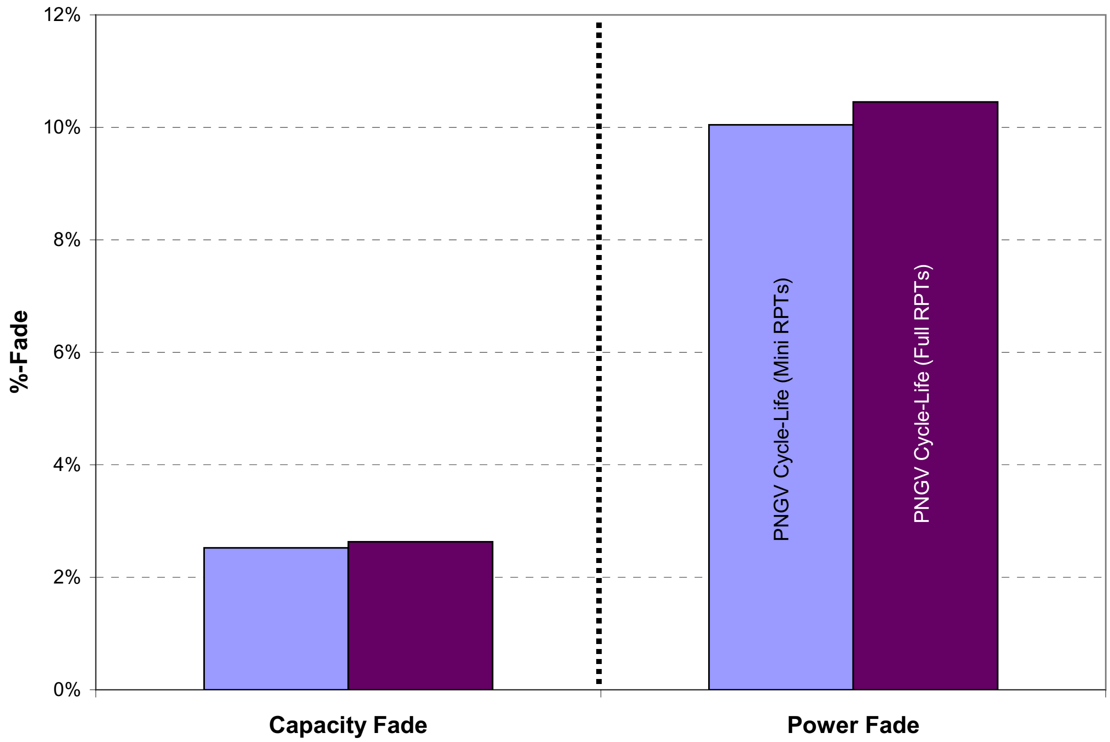

Figure 16. Average capacity and power fade for the full and mini-RPT groups

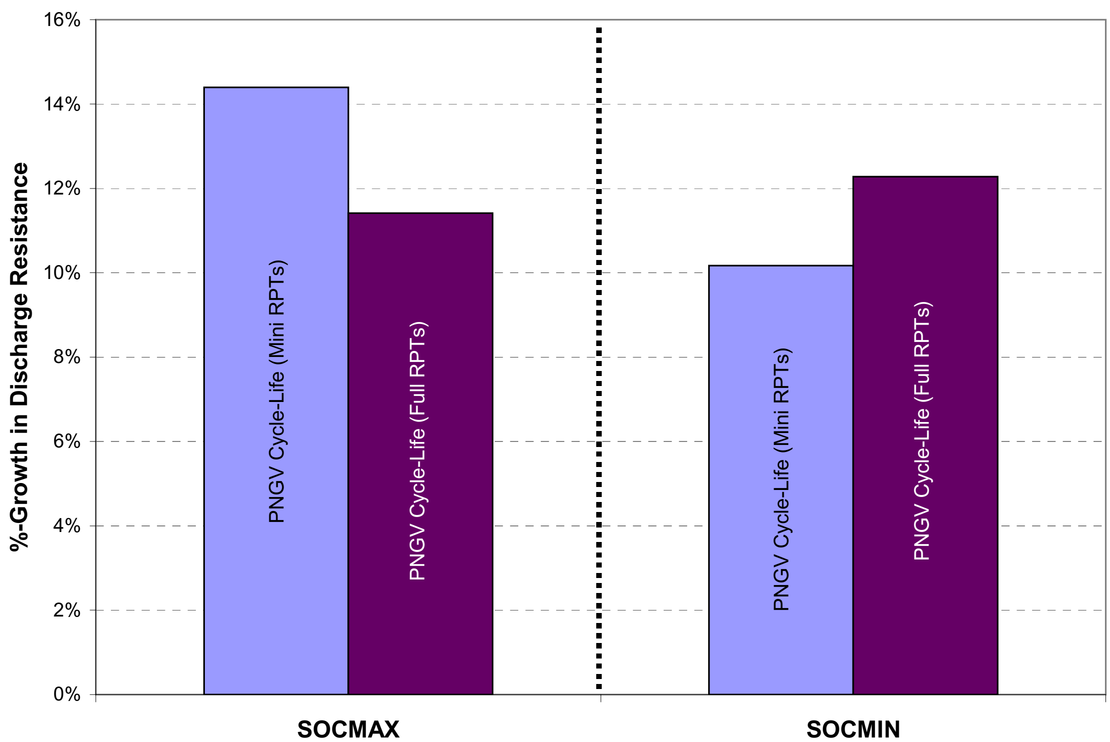

Figure 17. Average resistance growth for the full and mini-RPT groups

6. CONCLUSIONS

The Gen 2 Baseline and Variant C cells were life tested under various test temperature and SOC conditions. Every 4 weeks, reference performance tests were conducted to determine cell degradation as a function of test time. Although designed to be unobtrusive, the RPTs were causing discontinuities in the pulse resistance data, and appeared to contribute to cell degradation as well. Consequently, commercially available PowerfLite lithium-ion cells were purchased to study the impact of RPTs on life testing. Results from this study show that some components of the RPT were beneficial while other components were noticeably damaging. Cells subjected to more static capacity tests and lower temperatures at each RPT degraded more rapidly. The 25°C L-HPPC test was beneficial to cell performance. This is the most important component of the RPT since it provides information on power and energy for direct comparison with the established performance goals. EIS measurements were also beneficial to cell performance, but do not provide as much information about cell degradation. The MPPC was designed as an alternative that would still provides useful information on cell degradation while eliminating full charges and discharges. Preliminary investigations into the effect of the mini RPT show promising results.

7. FUTURE WORK

A more thorough investigation of the MPPC needs to be performed before it is implemented as a standard FreedomCAR reference performance test. This study needs to include long term life testing that compares mini and full RPT groups to a control group. The test matrix should include various temperatures and states of charge, particularly with variations on SOC_{MAX} and SOC_{MIN}. The study should also include an investigation of the impact of life predictions based on resistances from L-HPPC and MPPC profiles (see Figure 17). Finally, since the MPPC does not accurately provide the power at 300 Wh, an investigation of the effectiveness of estimating power with the MPPC also needs to be conducted.

8. REFERENCES

1. Tien Q. Duong et al., “Energy Storage Research & Development: 2003 Annual Progress Report,” U.S. DOE FCVT, May 2004.

2. *PNGV Test Plan for Advanced Technology Development Gen 2 Lithium-Ion Cells*, EVH-TP-121, Revision 6, October 2001.

3. *SNL Test Plan for Advanced Technology Development Gen 2 Lithium-Ion Cells*, SNL-ATD G2-TP, Revision 3, November 2002.

4. J. P. Christophersen, C. G. Motloch, I. D. Bloom, V. S. Battaglia, E. P. Roth, and T. Q. Duong, “Advanced Technology Development For Lithium-Ion Batteries: Gen 2 Performance Evaluation Interim Report,” INEEL/EXT-03-00095, February 2003.

5. *PNGV Battery Test Manual*, Revision 3, DOE/ID-10597, February 2001.

6. *Handbook of Batteries*. David L. Linden, ed., and Thomas B. Reddy, ed., 3rd ed., New York: McGraw Hill, 2002.

7. M.C. Smart, B.V. Ratnakumar, L. Whitcanack, K. Chin, M. Rodriguez, S. Surampudi, “Performance Characteristics of Lithium Ion Cells at Low Temperatures,” IEEE Aerospace and Electronic Systems Magazine, v. 17, n. 12, pp. 16-20, December 2002.

8. *Advanced Technology Development Program For Lithium-Ion Batteries: Battery Technology Life Verification Test Manual*, INEEL/EXT-04-01986, February 2005.

9. *FreedomCAR Battery Test Manual for Power-Assist Hybrid Electric Vehicles*, DOE/ID-11069, October 2003.

Appendix A

INL Test Procedure for an RPT Study Using the PowerfLite Cells

APPENDIX A

INL Test Procedure for an RPT Study Using the PowerfLite Cells (Pack 02)

Purpose

The intent of this testing is to determine what effect the reference performance tests (RPTs) have during aging using commercially available PowerfLite cells (Pack 02). The tests defined below will help isolate the most obtrusive component of the RPT sequence.

References

A. *PNGV Test Plan for Advanced Technology Development Gen 2 Lithium-Ion Cells*, EVH-TP-121, Revision 6, October 2001
B. *PNGV Battery Test Manual*, Revision 3, DOE/ID-10597, February 2001
C. EST Laboratory Standard Practices
D. IHRG# BAT-99-622 Battery and Capacitor Testing in the Energy Storage Technologies Laboratory.

Tests to be Performed

All testing will be performed in a thermal block using a rated capacity of 1.0 Ah and a voltage range of 4.2 to 2.75 V. The 24 PowerfLite flat cells will be split into various-size groups, as defined in Table 1a.

Table 1a. RPT Study Test Setup

# of Cells	Partial RPT	Temperature
4	Control	25°C
3	$C_1/1$	25°C
3	Static Capacity	25°C
4	$C_1/1$ and L-HPPC	25°C
3	$C_1/1$ and L-HPPC	0°C
4	EIS @ 60% SOC	25°C
3	EIS @ 100% SOC	25°C

Cycle-life testing will be performed at 60% SOC and 25°C, with partial RPTs (as defined in Table 1a) every 14 days. After a 14-day period, fully discharge the cells from ~60% SOC then fully charge them prior to beginning the partial RPT. The control cells will undergo continuous pulsing at 25°C without RPT interruptions. A soak period of 8 hours will be observed after a change in temperature. Detailed instructions for the partial RPTs are as follows:

1. **$C_1/1$:** Perform one $C_1/1$ static capacity discharge.
2. **Static Capacity:** Perform seven $C_1/1$ and one $C_1/25$ discharge, each followed by a $C_1/1$ charge.
3. **L-HPPC at 25°C:** Perform this test beginning with a $C_1/1$ discharge immediately prior to the L-HPPC pulses.

4. **L-HPPC at 0°C:** From a fully charged state, bring the cells to 0°C and temperature soak for 8 hours. At 0°C, perform this test beginning with a $C_1/1$ discharge immediately prior to the L-HPPC pulses.
5. **EIS @ 60% SOC:** From a fully charged state, discharge the cells to 60% SOC (3.859 V). Taper discharge at this voltage for a 2.5-hour total discharge. Rest at OCV for 12 hours prior to the EIS test.
6. **EIS @ 100% SOC:** Begin from a fully charged state, and rest at OCV for 12 hours prior to the EIS test.

The test sequence is as follows:

1. Perform a standard ATD Gen 2 cycle-life RPT (as defined in Reference A) to assess beginning-of-life conditions:
   a. 5 $C_1/1$ static capacity tests (verify that the last 3 are within ±2%).
   b. L-HPPC
2. Bring the cells to 60% SOC (3.859 V).
3. Perform an OSPS test scaled by a BSF of 2048 (as defined in Reference B), until the cells reach stable cycling. The control step will be applied to the discharge pulse.
4. Cycle-life test for 14 days using the standard 25-Wh Power Assist Cycle-Life Profile, as defined in Reference B.
5. For each cell group, perform the partial RPT defined in Table 1a at the specified temperature (the control cells will continue the special calendar-life test without RPT interruption).
   a. When a partial RPT is complete, immediately proceed with cycle-life testing. Do not wait for other partial RPTs to complete.
6. Bring the cells back to 60% SOC (3. 859 V).
7. Repeat Steps 4-6 for a total of at least 6 iterations.
8. Repeat Step 1 (with only 1 $C_1/1$ test) to assess end-of-life condition.